A1.1 1st Law- Internal energy depends on transferring of heat into or out of system, work done on or by system, adding or removing particles from system, work done by system = - work done on system | dQ: transfer of thermal energy between system and surroundings or between systems (heat), three types of heat conduction, convection, radiation| dW: transfer of kinetic energy through displacement due to some external force (work) many types of work: generalized work equation pressure work, gravitational, magnetic, electrical, ...| dD: transfer of energy through addition or subtraction of particles in system (diffusion)|many types of particle exchange interactions momentum transfer, thermal energy transfer ("mechanical"), chemical reactions, fusion, fission, electrostatic (polarization), most commonly encountered type of work – pressure work

State Functions- ΔQ, ΔW , not state functions process dependent ,changes in internal energy determinable but how much heat gained or work done not known from final conditions alone |ΔE, ΔN, ΔV – state functions, dE, dN, dV – exact differentials measurable, independent of process details, determined completely by initial and final conditions

Internal Energy-sum of all internal interactions and motions in a system, displacement away from equilibrium position with a fixed velocity results in restoring force due to interactions from neighbour take bonds as springs F = −κ ru(x) = u0 +1/2κ x2 each term represents a distinct way in which particle can store energy – degree of freedom, can be accessible or not accessible, each biξi2 =1v

Potential well-when more than one particle comes together, μ(J/mol or particle) : u0: potential energy reference level – major portion of chemical potential driving force for exchange of particles,u0 has a value if repulsive, u0 positive if attractive, u0 negative, u0: potential energy reference level depth depends on the strength of the interactions, the motion and spacings of particles system generally seeks to lower potential energy when particles are exchanged analogous to force in work systems, the exchange of particles is driven by the chemical potential, μdD =μdN, chem potential depends on depth of potential well for particle, u0 particle concentration by convention, energy transfer not due to heat or work determined by chemical potential, |μ for solids u0 << 0, and constant, for gases, u0 ≈ 0 (particles far apart), for solids, u0 << 0, and constant

Problem solving toolbox A1.1.1.2 • identify the system (of interest for problem), identify any assumptions (eg is it closed?), identify initial and final conditions, identify state functions

2nd Law as any large isolated system approaches equilibrium, the total number of available state increases, the total entropy increases even if not at equilibrium, as any large system approaches equilibrium, total number of available state increases system prefers to be in state where total accessible states are maximized system will adjust system variables(ε, V, N, p, μ, etc) to achieve maximization | Decrease ΔStotal = ΔSsystem + ΔSuniverse ( ) ≥ 0 Spontaneous/irrevisible/equilibrium

Fundamental Postulate - An isolated system in equilibrium is equally likely to be in any of its accessible microstates, Accessible states are the most probable macrostate with enough microstates, the total microstates is approximately the multiplicity of the most probable state. Only 2 conditions binomial coefficient small increase in number of microstates leads to massive increase in multiplicity highest multiplicity is most probable macrostate entropy must be maximum when interacting systems are in equilibrium

Microstates&CO related to entropy changes and energy through degrees of freedom, each possible organization of the system -> macrostate macrostates = N +1, each permutation of how that organization is achieved ->microstate Ω=ω^N, the number of microstates that belong to a particular macrostate -> multiplicity | Smallest possible microstate for particle defined by uncertainty of position and momentum ΔxΔp =h| V inc Ω inc| min # of mic is 1

Equipartition theorem interacting systems which share energy will try to maximize the total number of microstates spontaneous flow of energy stops when a system is at or very near its most probable macrostate from equipartition theorem, all particles have same probability of storing energy interactions, energy equally distributed over system, during interaction, tendency to share energy| Energy flows to equalize| spontaneous flow of energy stops when a system is at or very near its most probable macrostate

Entropy number of accessible states of system Ω (usual symbol S) is a measure of the number of specific realizations or microstates that may realize a thermodynamic system in a defined state specified by macroscopic variables. Most understand entropy as a measure of molecular disorder within a macroscopic system.|Reversibility; if system A + B -> <- C ΔS ≥ 0, at equilibrium, entropy is maximized, maximum number of accessible states

Thermodynamic Limit limit where measureable fluctuations away from the most likely macrostate never occur is the thermodynamic limit with enough microstates, the total microstates is approximately the multiplicity of the most probable state,

Problem solving toolbox A1.2.1 identify the system (of interest for problem) identify any assumption so if closed (no particle exchange therefore ΔN=0)o if statistically independent• identify initial and final conditions• identify state functions

3rd Law the entropy goes to zero as temperature goes to zero, no matter the values of external parameters pressure, volume, magnetic field, etc all other interactions do not vary with temperature, heat capacity goes to zero T → 0 ∴ Ω=1, Ω→ 1 ∴ S = 0

Equilibrium when probabilities of various states do not vary in time in a system in its own state of internal thermodynamic equilibrium, no macroscopic change in intensive properties occurs no net macroscopic flows of matter or of energy, either within a system or between systems time for the state to reach equilibrium |Equipartition energy will distribute to maximize the total number of microstates

Temperature&CO measure of change of entropy of system with energy temperature measure of microstate changes, experience of heat subjective, |triple point: solid, liquid, gas coexist at thermal equilibrium; cooling results in removal of heat energy reduction in number of accessible states reduction in degrees of freedom generally cannot treat as rigid point objects generally cannot neglect **interactions** negative values on K scale thermodynamically possible, not less than absolute zero, greater than infK, possible due to definition of T, negative T -> entropy decreases when energy is added, positive T -> entropy increases when energy is added. Strictly quantum.| temperature is a measure of energy stored in any degree of freedom,| cooling results in removal of heat energy, reduction in number of accessible states, reduction in degrees of freedom gauges: if can measure/calibrate properties of external system, can measure the properties of the systems of interest

Zeroth Law if two systems are in thermal equilibrium with a third system, they are also in thermal equilibrium with each other if two systems are in thermal/mechanical/diffusive equilibrium with a third system, they are also in thermal/mechanical/diffusive equilibrium with each other

Thermometer; scale totally arbitrary, externally calibrated measure of heat, heat subjective ∄ tie thermal measurement to mechanical change (volume expansion) volume change due to difference in thermal expansion coefficient for different materials, volume change related to density of material Thermometer experience of temperature subjective scale totally arbitrary need link to easily measure property

Thermal Energy energy given by motions and positions (i.e. given by degrees of freedom) of a particle collectively referred to as thermal energy

Heat Capacity change of heat with change of temperature, heat energy required to make small change in T, due to first law, measurement conditions critical ,other interactions possible with change in heat, rarely consider ΔN, Δμ, Δv, heat capacity not defined at phase transitions as energy change with no change in temperature focus on mechanical interactions – p or V heat capacity – indication of system response to changes in temperature, materials with low specific heat capacity warm and cool quickly -> need less heat energy for a given change in temperature materials with high specific heat capacity take a long time to warm up and retain their heat for a long time. volume heat capacity directly proportional to degrees of freedom, low values of C mean that small changes in energy can cause large changes in temperature

Problem solving toolbox B1.1.-ss identify the system (of interest for problem) • identify any assumptions o if closed (no particle exchange therefore ΔN=0)o if statistically independent, if distinguishable – affects the number of microstates , if equilibrium• identify initial and final conditions• identify state functions• identify fundamental thermodynamic tools/equations applicable to problem.

Models-models allow qualitative understanding and easy calculation, generally idealized, typically number of parameters less than types of interactions system characteristics (E, Cv, Cp, β,...) influenced by system parameters (p, T, V, N, ...), interrelationships are called equations of state

Ideal gas; assumptions atoms, molecules, particles, etc of ideal gas are rigid spheres (only elastic scattering) only point particles no long range interaction between particles at long distances, all energy is kinetic DOF: ideal gas assumes rigid objects with no volume, volume of gas independent of volume of particle ,point particles can come infinitely close together

Real gas not strictly v=3 – rotations, vibrations, etc of molecules real gases repel each other below equilibrium distance need to make correction for excluded volume real gases attract each other at long separations need to make correction for pressure changes with increased interaction effective pressure, pressure correction due to attractive tail at long distance

Volume effects as gas molecules come close together (i.e as pressure increases), gas will eventually liquify compressibility of liquids low compared to gases

Natural Constraints based on thermodynamic laws and effects of Equilibrium five types, first law: conservation of energy, second law: maximization of entropy, deviations from equilibrium, third law: S -> finite value as T -> 0, interrelationships E + PV −TS ≡G

Problem solving toolbox A1.3. identify the system (of interest for problem), identify any assumptions (eg is it closed?), identify initial and final conditions, identify state functions identify fundamental thermodynamic tools/equations applicable to problem, reduce variables apply natural constraints manipulate partial derivatives into easily measureable forms apply models

Reduction of Variables- use basic tools of thermodynamics (laws, state f, fundamental postulate, etc) 2. reduce number of independent variables, three major ways to reduce variables 1. specific models for relationships between parameters 2 natural constraints 3 imposed constraints

Imposed Constraints constraints imposed by how we formulate problem or from the limitations of the experimental set-up

Interrelationships Thermodynamic potentials by assuming interaction with reservoir (ie the universe) under various conditions, Helmholtz free energy, F (neglect p, N), Gibb's free energy, G (exchange of E and V), Enthalpy, H (constant S), Integrated energy, E (nothing constant)

Natural Variables for a given function, variables that if defined yield unique value for other thermodynamic variables

$dE_{internal} = TdS - pdV + \mu dN$

$dE_{integrated} = TdS + SdT - pdV - Vdp + \mu dN + Nd\mu$

liquids, atomic gases, diatomic gases, solids

$\omega = \frac{L_x L_{p_x}}{h}$ area of one state $\Delta x \Delta p_x = h$

$S \equiv k \ln \Omega$

$\frac{N_{V_1}}{E_1} = \frac{N_{V_2}}{E_2}$

$\omega = \frac{V_r V_p}{h^3}$

$\omega = \int \frac{dxdydz \cdot dp_x dp_y dp_z}{h^3}$

$dE = \sum_i dQ_i - \sum_i dW_j + \sum_i dD_i$

replace inexact differentials with exact ones

$dW = \Im du$

$dE = \sum_i dQ_i - pdV + \sum_i dD_i$

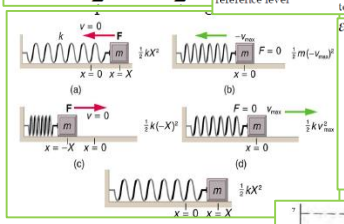
Correct Answer: $u(xyz) = u_0$, $u(xyz) = 0$, $u(xyz) = \frac{1}{2}\kappa x^2 + \frac{1}{2}\kappa y^2 + \frac{1}{2}\kappa z^2$

$u(xyz) = u_0 + \frac{1}{2}\kappa x^2 + \frac{1}{2}\kappa y^2 + \frac{1}{2}\kappa z^2$

Potential energy

$u(x) = u_0 + \frac{1}{2}\kappa x^2$

reference level — potential due to interaction



$\varepsilon = \varepsilon_{translation} + \varepsilon_{rotation} + \varepsilon_{vibration}$

$\varepsilon_{translation} = \frac{1}{2m} p_x^2$

$\varepsilon_{rotation} = \frac{1}{2I_y} L_y^2$

$\varepsilon_{vibration} = \frac{1}{2}\kappa x^2 + \frac{1}{2m} p_x^2$

if you know the number of energy levels occupied and the number of potential occupiers

$M_{ar} = \frac{N!}{\prod_{i=1}^{N} n_i!}$

if you only know the energy per particle,

$\omega = (const)\varepsilon^{N_f/2}$

$\Omega = (const)E^{N_f/2}$

$a^x = 10^{x \log_{10}(a)}$ $\ln(1+\varepsilon) \approx \varepsilon$ (for $\varepsilon \ll 1$)

$e^x = 10^{0.434x}$ $(1+\varepsilon)^x \approx e^{\varepsilon x} = 10^{0.434\varepsilon x}$ (for $\varepsilon \ll 1$)

$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{V,E} dV + \left(\frac{\partial S}{\partial N}\right)_{E,N} dN$

change of entropy with energy $\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$

change of entropy with volume $\left(\frac{\partial S}{\partial V}\right)_{E,N} =$

change of entropy with number of particles $\left(\frac{\partial S}{\partial N}\right)_{E,V} =$

- intensive variables are equal
  - $T_1 = T_2$
  - $p_1 = p_2$
  - $\mu_1 = \mu_2$
- extensive variables are summed
  - $S_0 = S_1 + S_2$
  - $V_0 = V_1 + V_2$
  - $N_0 = N_1 + N_2$

$E = Nv(\varepsilon_{DOF})$
$= Nv(b_i \xi_i^2)$
$= N\bar{\varepsilon}$

$dz = \frac{\partial z}{\partial x}\Big|_y dx + \frac{\partial z}{\partial y}\Big|_x dy$

$z = \frac{\partial z}{\partial x}\Big|_y x + \frac{\partial z}{\partial y}\Big|_x y$

inverse rule: $\frac{\partial y}{\partial x} = \left[\frac{\partial x}{\partial y}\right]^{-1}$

cyclic rule: $\frac{\partial x}{\partial y}\Big|_z \frac{\partial y}{\partial z}\Big|_x \frac{\partial z}{\partial x}\Big|_y = -1$

chain rule: $\frac{\partial x}{\partial y}\Big|_z = \frac{\partial x}{\partial T}\Big|_z \frac{\partial T}{\partial y}\Big|_z$

ideal gas

isothermal	$pv - RT = const$
isobaric	$\frac{v}{T} = \frac{R}{p} = const$
isochoric	$\frac{p}{T} = \frac{R}{v} = const$
adiabatic	$pV^\gamma = const$
	$V^{\gamma-1}T = const$

- van der Waals gas:

isothermal	$\left(p - \frac{a}{v^2}\right)(v-b) = RT = const$
isobaric	$\frac{T}{v-b} - \frac{a}{Rv^2} = \frac{p}{R} = const$
adiabatic	$\left(p + \frac{a}{v^2}\right)(v-b)^\gamma = const$
	$(v-b)^{\gamma-1}T = const$

- adiabatic processes
  - increased volume causes decreased temperature
  - increased pressure causes increased temperature
  - increased pressure causes decreased volume

$\Omega_{ideal\ gas} = (const)V^N E^{3N/2}$

$S_{ideal\ gas} = k \ln \Omega_{ideal\ gas} = (const) + Nk \ln V + \frac{3}{2} Nk \ln E$

→ ideal gas law demonstrates equipartition

$S_{ideal\ gas} = (const) + Nk \ln V + \frac{3}{2} Nk \ln E$

$\left.\frac{dS_{ideal\ gas}}{dE}\right|_{V,N} = \left.\frac{d}{dE}\right|_{V,N} \left((const) + Nk \ln V + \frac{3}{2} Nk \ln E\right) = \frac{3}{2}\frac{Nk}{E}$

$\left.\frac{dS_{ideal\ gas}}{dE}\right|_{V,N} = \frac{1}{T}$

$E = \frac{3}{2} NkT$

$E = \frac{\nu}{2} NkT + N\mu$

assuming an ideal gas density of states yields three fundamental equations for ideal gases

$E = \frac{3}{2} NkT$ $\quad -\frac{\partial S}{\partial \varepsilon} = \frac{1}{T}$

$pV = NkT$

$\frac{\partial S}{\partial V} = \frac{p}{T}$ $\quad \mu = -kT\left(\ln\left[\frac{2}{3p}\right] + \frac{5}{2}\ln E\right)$ $\quad \frac{\mu}{T} = -\frac{\partial S}{\partial N}$

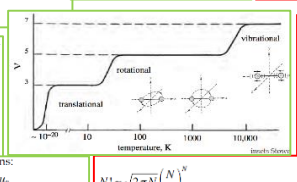
relates macroscopic properties (p, V, T) directly to DOF

energy can be expressed in a general harmonic form

$\varepsilon_i = b_i \xi_i^2$ (constant; position or momentum coordinate)

energy as sum of equivalent variables

$\varepsilon_{internal} = \sum_i b_i \xi_i^2 + u_0$



- p_s is the probability that the criterion is satisfied (i.e. takes a particular value) and
- p_f is the probability that it is not satisfied (p_s=1-p_f),

then for N elements, the probability of n elements fulfilling that criterion

$P_N(n) = \frac{N!}{n!(N-n)!} p_s^n p_f^{N-n}$ (2.4)

$\Omega_0 \approx M_0(N,n) = \frac{N!}{n!(N-n)!}$

Microstates and entropy changes

$\Delta S = k \Delta \ln \Omega$

$\frac{\Omega_2}{\Omega_1} = \exp\left(\frac{\Delta S}{k}\right)$

$\frac{\Omega_2}{\Omega_1} = \exp\left(\frac{\Delta E + p\Delta V - \mu\Delta N}{kT}\right)$

$v = \frac{V}{n}$

v: molar volume

probability that system is in a given state

$P_s = C \exp\left(-\frac{\Delta E + p\Delta V - \mu\Delta N}{kT}\right)$

$pV = NkT$

$pV = nRT$

$R = kN_A = 8.31 \frac{J}{K \cdot mol}$

R=ideal gas constant
n=number of mol

$\frac{P_1}{P_0} = e^{-1}$

$\frac{\varepsilon_2 - \varepsilon_0}{kT} = 1$

$T_e = \frac{\varepsilon_1 - \varepsilon_0}{k}$

Ideal gas work and hea

in isothermal conditions (i.e. dT=0)

$\Delta w = kT \ln\left(\frac{v_2}{v_1}\right)$

Δε=0 as it only depends on T (Δε=3/2kΔT)

$\Delta w = kT \ln\left(\frac{V_2}{V_1}\right) = \Delta q$

$\beta = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_p$

$pv = NkT$

$V = \frac{NkT}{p}$

$\left.\frac{\partial V}{\partial T}\right|_p = \frac{Nk}{p} \rightarrow \beta = \frac{1}{T}$

$K_{ideal\ gas} = \frac{1}{p}$

- total energy for a particle in three dimensions: (monatomic system) $\varepsilon_{internal} = \sum_i b_i \xi_i^2 + u_0$

$\varepsilon = \frac{1}{2m} p_x^2 + \frac{1}{2m} p_y^2 + \frac{1}{2m} p_z^2$ (4.5)

$\varepsilon = u_0 + \frac{1}{2m} p_x^2 + \frac{1}{2m} p_y^2 + \frac{1}{2m} p_z^2$ (4.4)

$\varepsilon = u_0 + \frac{1}{2}\kappa x^2 + \frac{1}{2}\kappa y^2 + \frac{1}{2}\kappa z^2 + \frac{1}{2m} p_x^2 + \frac{1}{2m} p_y^2 + \frac{1}{2m} p_z^2$

$N! \approx \sqrt{2\pi N}\left(\frac{N}{e}\right)^N$ (2.5a)

$\ln(N!) = N \ln N - N + \frac{1}{2}\ln(2\pi N)$ (2.5b)

$N! = e^{N \ln N - N}$ for sufficiently large N

- small systems: binomial distribution
- large systems: Gaussian distribution

$P_N(n) \approx \frac{N!}{n!(N-n)!} p_s^n p_f^{N-n}$ $\quad P(E_1) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(\varepsilon_1 - \bar{\varepsilon}_1)^2}{2\sigma^2}}$

$\sigma = \sqrt{\frac{2\bar{E}_1(E_0 - \bar{E}_1)}{(Nv)_0}}$

if know heat capacity and temperature change, can use heat capacity to define entropy change of system

$\Delta S = \int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{C_v dT}{T}$

$C_V = \left.\frac{\partial Q}{\partial T}\right|_V$ $\quad C_p = \left.\frac{\partial Q}{\partial T}\right|_p$

$C_V = \frac{\nu}{2} Nk$ $\quad C_p = \frac{\nu}{2} Nk + p\left.\frac{\partial V}{\partial T}\right|_p$

constant volume with heat; pressure changes

constant pressure with heat; volume changes

Energy changes with temperature

$E = N\mu + \frac{Nv}{2} kT$

how does energy change with temperature?

$dE = d\left(N\mu + \frac{Nv}{2} kT\right)$

$dE = \mu dN + N d\mu + \frac{\nu}{2} kT dN + \frac{\nu}{2} kT d\nu + \frac{N\nu}{2} kdT$

$dE = dQ - pdV + \mu dN$

$dQ = N\mu d\nu + \frac{\nu}{2} kT dN + \frac{\nu}{2} kT d\nu + \frac{N\nu}{2} kdT + pdV$

$C_\nu = \frac{dQ}{dT} = N\mu \frac{\partial \nu}{\partial T} + \frac{\nu}{2} kT \frac{\partial N}{\partial T} + \frac{\nu}{2} kT \frac{\partial \nu}{\partial T} + \frac{N\nu}{2} k + p\frac{\partial V}{\partial T}$

$C_v = \frac{\nu}{2} Nk + p\left.\frac{\partial V}{\partial T}\right|_v + N\left.\frac{\partial \mu}{\partial T}\right|_v + \frac{N}{2} kT \left.\frac{\partial \nu}{\partial T}\right|_v + \frac{\nu}{2} kT \frac{\partial N}{\partial T}$

gases:

$C_v = \frac{\nu}{2} Nk$ (10.13)

$C_p = \frac{\nu}{2} Nk + p\left.\frac{\partial v}{\partial T}\right|_p$ (10.15)

ideal gas:

$c_v = \frac{3}{2} R$

$c_p = \frac{3}{2} R + R = \frac{5}{2} R$

$0 = SdT - Vdp + Nd\mu$

$Nd\mu = -SdT + Vdp$

relates intensive variables

no intensive variables can be changed alone

$b_i \xi_i^2 = \frac{1}{2} kT$

$C_y' = \frac{1}{n} C_y$ molar heat capacity

$c_y = \frac{1}{m} C_y$ specific heat capacity

$P_i = Ce^{-\frac{\varepsilon_i}{kT}}$ $\quad P_j = Ce^{-\frac{\varepsilon_j}{kT}}$

assuming C same in both cases

$\frac{P_j}{P_i} = \frac{Ce^{-\frac{\varepsilon_j}{kT}}}{Ce^{-\frac{\varepsilon_i}{kT}}} = e^{-\frac{(\varepsilon_j - \varepsilon_i)}{kT}}$

if energy spacing is $\varepsilon_1 - \varepsilon_0$ between ground state (ε_0) and first excited state (ε_1)

- $\varepsilon_1 - \varepsilon_0 > kT$: implies low probability of excitation
- $\varepsilon_1 - \varepsilon_0 < kT$: implies high probability of excitation

$E = TS - pV + \mu N$

Thermodynamic potentials by assuming interaction with reservoir (ie the universe) under various conditions

- Helmholtz free energy, F (neglect p, N) $F \equiv E - TS$
- Gibb's free energy, G (exchange of E and V) $G \equiv E\nu - TS = H - TS$
- Enthalpy, H (constant S) $H \equiv E + p\nu$
- Integrated energy, E (nothing constant)

relationships between p, V, and T are called equations of state

$pV = nRT$ ideal gas

$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$ vdW gas

3) deviations from equilibrium: act to restore equilibrium

$dS_0 = \frac{1}{T_0}\left[\left(\frac{T_2 - T_1}{T_1}\right) dQ_1 + (p_1 - p_2) dV_1 - (\mu_1 - \mu_2) dN_1\right]$

$dS_0 > 0$

- thermal interactions: if heat is added to a system, T increases $dTdQ > 0$
- mechanical interactions: if volume is increased, p decreases $dpdV < 0$
- diffusive interactions: if particles are added, μ increases $d\mu dN > 0$

Equipartition

Boltzmann statistics

Classical description

- distinguishable particles with given energy

fixed number of particles, ΔN=0, many different energy states

$P_s = Ce^{-\frac{1}{kT}(\Delta E - p\Delta V)}$

$p\Delta V = 10^{-6}$ eV $\quad kTRoom = 0.026$ eV

$P_s \approx Ce^{-\frac{\varepsilon_s}{kT}}$ $\quad p\Delta V \ll \Delta E$

control internal energy through T

- ability of individual particles to take one particular energy

Quantum statistics

quantum state identified by fixed volume in phase space

$\omega = \frac{V_{phase\ space}}{V_{one\ state}}$ $\quad \omega = \frac{V_r V_p}{h^3}$

system exchanges particles with the reservoir

$\Delta N = n, \Delta E = n\varepsilon, \Delta V = 0$

$P_s = Ce^{-\frac{n}{kT}(\varepsilon - \mu)}$

control system through μ

- ability of quantum state to accommodate particles

Specific potentials

thermodynamic potential	natural variables	derived variables	differential form
specific internal energy, e	s, v	$T, -p$	$de = Tds - pdv$
specific Helmholtz free energy, f	T, v	$s, -p$	$df = -sdT - pdv$
specific enthalpy/ specific heat, h	s, p	T, v	$dh = Tds + vdp$
specific Gibb's free energy, g	T, p	$-s, v$	$dg = -sdT + vdp$

- interrelationships through permutations

thermodynamic potential	natural variables	differential form
entropy, S	$s = \frac{S}{N}, v = \frac{V}{N}$	$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$
internal energy, E		$dE = TdS - pdV + \mu dN$
Helmholtz free energy, F	T, V, N	$dF = -SdT - pdV + \mu dN$
Enthalpy, H	S, p, N	$dH = TdS + Vdp + \mu dN$
Gibb's free energy	T, p, N	$dG = -SdT + Vdp + \mu dN$

Q13. On a hot summer day, a student turns a fan on when leaving the room in the morning. Upon returning, will the room be warmer or cooler than the neighboring rooms? Explain. Assume all doors and windows are kept closed

The room gets warmer than other rooms. The room is a closed system, by the first law of thermodynamics, $dE=dQ-dW+\mu dN$, $\mu dN=0$. There is heat transfer from outside to the room, so dQ>0. The only work done in the room is supplied by the fan, so dW<0. Hence while other rooms only have dE=dQ, this room with a fan has extra energy dE=dQ+dW, so it gets warmer because of the fan.

Consider the process of heating water in a pan on top of an electric range until boiling in a insulated room. A) type of system?|Isolated system. B) Assumptions to solve| room is closed, no energy leaving or entering system. C)Identify all forms of energy| Thermal energy and electric work. D) isolated system therefore no change in internal energy.

A gas spring, with C=200Nm$^{1.4}$ and k=1.4, is heated by a burner from below while changing distance from 0.2 m to 0.7 m. During the process 50kJ of heat is transferred to the gas and 3 kJ is lost to the surrounding air. What is the change in energy?

$\Delta E = 47.62$ kJ

$\Delta E = \Delta Q - \Delta W + \Delta \cancel{PV}^{0}$

$\Delta Q = 50\text{kJ} - 3\text{kJ}$

$\Delta W = \int F\,dx = \int_{0.2}^{0.7} \frac{C}{x^{1.4}}\,dx = -375$ kJ

Dohr

$\nu = 6$

if we have 5 particles $\Rightarrow \mu\nu = 5(6) = 30$

$\epsilon_2 = 1.29\,\epsilon_1$

$\Omega \propto \epsilon^{\mu\nu_2}$

$\frac{\Omega_2}{\Omega_1} = \left(\frac{\epsilon_2}{\epsilon_1}\right)^{\mu\nu_2}$

$\frac{\Omega_2}{\Omega_1} = 3\text{e}$

Table of thermodynamic properties

@ 298K, 1 atm

Substance (form)	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	S (J/K)	C_P (J/K)	V (cm^3)
H_2 (g)	0	0	130.68	28.82	
H^+ (aq)	217.97	203.25	114.71	20.78	
H_2O (l)	0	0	69.91	75.29	18.068
H_2O (g)	−285.83	−237.13	188.83	33.58	
He (g)	−241.82	−228.57	126.15	20.79	
Hg (l)	0	0	76.02	27.98	14.81
N_2 (g)	0	0	191.61	29.12	
NH_3 (g)	−46.11	−16.45	192.45	35.06	
Na^+ (aq)	−240.12	−261.91	59.0	46.4	−1.2
NaCl (s)	−411.15	−384.14	72.13	50.50	27.01
$NaAlSi_3O_8$ (albite)	−3935.1	−3711.5	207.40	205.10	100.07
$NaAlSi_3O_8$ (jadeite)	−3030.9	−2852.1	133.5	160.0	60.40
Ne (g)	0	0	146.33	20.79	
O_2 (g)	0	0	205.14	29.38	
O_2 (aq)	−11.7	16.4	110.9		
OH^- (aq)	−229.99	−157.24	−10.75	−148.5	

$S = \int_0^{298} \frac{C_p}{T}\,dT$

$\Delta S = S_{H_2} + \frac{1}{2}S_{O_2} - S_{H_2O}$

$= 168.34$ J/K

$T\Delta S = 48.\cancel{76}$ kJ

$\Delta G = 285.83 - 48.\cancel{76}$

$= 237.15$ kJ

What is ΔG (i.e. electrical energy input) for hydrolysis of water?

$G = E + pV - TS \rightarrow \Delta G = \Delta E + p\Delta V - T\Delta S$

Schroeder appendix

Constrained processes

Table 13.1. ΔE, ΔW, ΔQ ($\Delta E = \Delta Q - \Delta W$), and ΔS *for an ideal gas operating under various constraints*

Quantity	Isobaric	Isochoric	Adiabatic*	Isothermal
ΔE	$nC_V\Delta T$	$nC_V\Delta T$	$nC_V\Delta T$	0
ΔW	$nR\Delta T$	0	$-nC_V\Delta T$	$nRT\ln\left(\frac{V_f}{V_i}\right)$
ΔQ	$nC_p\Delta T$	$nC_V\Delta T$	0	$nRT\ln\left(\frac{V_f}{V_i}\right)$
ΔS	$nC_p\ln\left(\frac{T_f}{T_i}\right)$	$nC_V\ln\left(\frac{T_f}{T_i}\right)$	0	$nR\ln\left(\frac{V_f}{V_i}\right)$

Helpful relationships (ν = number of degrees of freedom per molecule, $C_{V,p}$ are the molar heat capacities)

$pV = nRT, \quad E = nC_VT, \quad C_V = (\nu/2)R, \; C_p = C_V + R, \quad \gamma = C_p/C_V = (\nu+2)/\nu$

Other variables The following relationships may be used to exchange variables in the above expressions:

	isobaric	isochoric	adiabatic	isothermal
$T =$	$\left(\frac{p}{nR}\right)V$	$\left(\frac{V}{nR}\right)p$	$pV^\gamma = \text{const.}$	$V = \frac{nRT}{p}$
	$\frac{T_i}{T_f} = \frac{V_i}{V_f}$	$\frac{T_i}{T_f} = \frac{p_i}{p_f}$	$TV^{\gamma-1} = \text{const.}$	$\frac{V_i}{V_f} = \frac{p_i}{p_f}$

* For adiabatic processes, $\Delta W = -\Delta E = -nC_V\Delta T = \int p\,dV = [1/(\gamma-1)](p_iV_i - p_fV_f)$.

ideal gas relations for constrained processes

Q7. Stowe problem 10.49: An equation of state for a certain material is found to be $pV^2 - aTV = bT$, where a and b are constants. In terms of p, V, T, find (a) the coefficient of thermal expansion, (b) the isothermal compressibility.

Write the differential form of the equation of state; $V^2dp+(2pV-aT)dV-(aV+b)dT=0$

a) for β take the derivative of the equation with respect to T (i.e. divide all variables by dT) with p fixed β=(a+b/V)/(2pV-aT) b) for k do the same except with respect to V with T fixed, κ=V/(2pV-aT)

Stowe problem 8.3: Consider a system A_0 composed of subsystems A_1 and A_2 in thermal equilibrium. The number of states accessible to each increases with it energy according to $\Omega_1=(E_1/C)^{10}$, $\Omega_2=(E_2/C)^5$ where $C=10^{-23}$ J. The total energy of the combined system is fixed at $E_0 = E_1 + E_2 = 10^{-18}$ J.

(a) How many degrees of freedom have systems A_1 and A_2, respectively

(b) Use the fact that $\delta\Omega_0/\delta E_1 = 0$ when Ω_0 is a maximum to find E_1 and E_2 when the combined system is in equilibrium?

(c) What is the entropy of the combined system in equilibrium?

(d) Using the definition of temperature, and the fact that in equilibrium the temperature of either system is the same, find the temperature of the system

a) 20, 16

b) $\Omega_0=\Omega_2\Omega_1$ $d\Omega_0/dE_1=(d\Omega_1/dE_1)\Omega_2+(d\Omega_2/dE_1)\Omega_1$, $E_2=E_0-E_1$,
therefore $E_1=5.56\text{x}10^{-19}$ J, $E_2=4.44\text{x}10^{-19}$ J

c) $S_0=k\ln\Omega_0=2.7\text{x}10^{-21}$ J/K

d) $dS/dE=1/T$, can solve for E=(Nν/2)kT at equilibrium, T=4020 K

ter a long trip, tire pressure typically increases. How n we explain this behaviour?

$dN = 0$

$dN = 0 \quad \Delta p = 10$ kPa

$\frac{P}{T} = \frac{Nk}{V}$ $\quad p_i = 210$ kPa

$\frac{P_1}{T_1} = \frac{P_2}{T_2} \rightarrow \frac{T_2}{T_1} = \frac{P_2}{P_1} = \frac{220\text{ kPa}}{200\text{ kPa}}$

$T_1 = 298 \rightarrow T_2 = 312.8$ K $\rightarrow$

$\mu = -kT\left[\ln\frac{2}{q_i}\frac{3}{2} + \frac{5}{2}\right]$ $\quad \epsilon = \frac{3}{2}kT$

$= -kT\left[\ln\frac{2}{q_i}\frac{3}{2} + \frac{5}{2}\right]$

$= -0.351$ eV

Q16. Stowe problem 3.18: Suppose that we have 10 000 spin-1/2 particles, which are either spin up or spin down. Thermal agitation causes them to flip around, so that any one particle spends roughly half the time up and half down. On average, at any instant there will be 5000 up and 5000 down.

(a) What is the standard deviation for fluctuations around this value?

(b) What is the probability that at a given instant there are exactly 4900 up and 5100 down?

(a) The probability of a particle spin-up is p=1/2, spin-down is q=p-1=1/2, and N=10000

The standard deviation is given by (3.4) $\sigma = \sqrt{Npq} = \sqrt{10000\times\frac{1}{2}\times\frac{1}{2}} = 50$

(b) using equation (3.7) $P(n) = \frac{1}{\sqrt{2\pi}\sigma}e^{-(n-\bar{n})^2/2\sigma^2}$

$P(4900) = \frac{1}{\sqrt{2\pi}\times 50}e^{-100^2/(2\times 50^2)} \approx 0.0011$

Material melting contradicting 2nd law as adding heat reduces # of states
How energy relates to the number of states
When solid turns to liquid, each molecule gains access to much larger volume in coordinate space pace-2nd LAW:reduction in states means reduction in entropy –which is contrary tothe 2ndlaw as heat is added
Molecules are now mobile and can move through the system-The additional states from the increased accessible volume that a molecule has access to outnumber the states available in the potential energy degrees of freedom.
This increase in mobility per particle gives them each more accessible states.

Q11. Stowe problem 7.5: Consider a system A_0 composed of subsystems A_1 and A_2 for which the number of degrees of freedom are 4 and 6, respectively. Energy comes in units of 1 and the energy of the combined system is 6.

(a) Construct a table like Table 7.1 or 7.2 illustrating the seven possible energy distributions for the system and Ω_1, Ω_2, and Ω_2 for each.

(b) Which distribution of energies is most probable, and what is the probability for this distribution?

a)

E_1	E_2	Ω_1	Ω_2	Ω_0
0	6	0	216	0
1	5	1	125	125
2	4	4	64	256
3	3	9	27	243
4	2	16	8	128
5	1	25	1	25
6	0	36	0	0
			Total =	777

b) The distribution of energies that is most probable is (2,4) since it has the largest Ω0. The probability for this distribution is 256/777 = 0.33.

If we take 2 large interacting systems

$E_0 = 5 \quad N_1 = 3\text{x}10^{24} \quad N_2 = 5\text{x}10^{24}$

$\Omega(A_1) \cong 10^{0.9\text{x}10^{24}}$

$\Omega(A_2) \cong 10^{2.39\text{x}10^{24}}$

$S_1 = k_B\ln\Omega_1 = k_B\ln\left(10^{0.9\text{x}10^{24}}\right) \approx k(9\text{x}10^{23})$

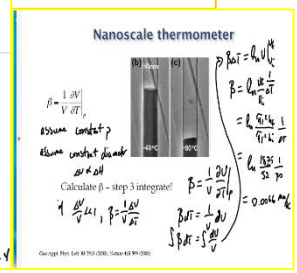
$S_2 = k(2.39\text{x}10^{24})$

$S_1 = (1.38\text{x}10^{-23})(9\text{x}10^{23}) = 12.4$

$S_2 = 32.\cancel{9}$

$\Omega_0 = \Omega_1\Omega_2$

$S_0 = k_B\ln\Omega_0 = k_B\ln 10^{3.29\text{x}10^{24}} = 45.4$



Consider two gases, one hot one cold brought together in an isolated container, a) why is statistical methods needed as proof of the 2ndlaw, b) Does the 2nd law require that the decrease in energy of the gas to be equal to the increase in the cold one?

The Main idea that needed to be expressed is that the way heat transfer works between a warmer and colder gas is that the molecules of the warmer gas have, on average, more kinetic energy. These particles transfer some of this energy when they collide with the particles of the colder gas, as they generally have lower kinetic energy. Since particles have a range of energies, some individual particles from the colder system may transfer energy to particles of the hotter system, but we must consider the average. Since there are very large numbers of collisions that determine the ultimate transfer of heat and energy, the process must be described statistically. Identify that, since entropy is not a conserved property, it is not true that entropy gained by one system is necessarily lost by the other or vice versa. Must discuss that entropy is maximised at thermal equilibrium, therefore since the combined system is not initially in equilibrium when the two individual systems are brought into contact, total entropy must increase.

$\Omega(\mu,\nu) = C(N,\nu)V^N\epsilon^{\mu\nu_2}$

$\Delta S = k_B\ln\Omega_2 - k_B\ln\Omega_1$

$= k_B\ln\left(\frac{\Omega_2}{\Omega_1}\right)$

$= k_B\ln\left[\frac{C(\mu,\nu)(2v)^{N}\,\epsilon^{(\text{kg}\cdot\text{m}^2/\text{s}^2)(\text{C})}}{C(\mu,\nu)V^{N}\epsilon^{(\text{kg}\cdot\text{m}^2/\text{s}^2)\frac{3}{2}}}\right]$

Entropy

- Consider a liquid that has the following energy levels. What is the change in entropy per unit volume if 10^{23} molecules are excited to T=320 K?

Motion energy levels

$\Delta\epsilon_i = h\cancel{f}$ ——— $f_{vib(internal\ in\ one\ liquid\ molecule)} = 1.2\text{x}10^{14}$ Hz, T=5694 K

——— $f_{vib}(y,z)$ $6.3\text{x}10^{12}$ Hz, T 299 K

——— f_{rot} (x) = $7.1\text{x}10^{12}$ Hz, T=337 K

——— f_{trans} (x,y,z) = $5.75\text{x}10^{12}$ Hz, T=273 K

——— $f_{vib(between\ frozen\ liquid\ molecules)}$ = $1.4\text{x}10^{11}$ Hz; T 6.64 K

$\Delta\Omega = C\Delta\epsilon^{\mu\nu_2}$

$C(N,N) \cong 10^{23}$

$y = mx + b$ $\quad \frac{\Delta\epsilon_2 - \Delta\epsilon_1}{T_2 - T_1}$ $\quad \Delta\epsilon(320) = 9.44\text{x}10^{-21}$ J

$\Delta\Omega = 10^{23}\left(9.44\text{x}10^{-21}\right)^{2.5\text{x}10^{23}}$

$\Delta S = k_B\Delta\Omega$

Final example

System : gas + reservoir

State variables: v, T

$v_i = 0.001$ m^3/mol $\quad T = T_{reservoir}$

$v_f = 0.040$ m^3/mol

per mol ∴ ΔW not relevant

$p = \frac{RT}{v-b} - \frac{a}{v^2}$

v, T given/known ∴ want to convert $\epsilon(\mu,\nu) \rightarrow \epsilon(T,v)$

$d\epsilon = \frac{\partial\epsilon}{\partial T}\Big|_v dT + \frac{\partial\epsilon}{\partial v}\Big|_T dv$

T const

$\therefore d\epsilon = \frac{\partial\epsilon}{\partial v}\Big|_T dv$

Knowing that $d\epsilon = TdS - pdv$ we replace $d\epsilon$

Final example

Propane gas is expanded from 0.001m^3/mol to 0.040 m^3/mol while in contact with a hot reservoir at 100°C. The expansion is not reversible (i.e. ΔS>0, dq≠ds). The heat extracted from the bath is 600 J/mol. What is the work done by the gas if the pressure is given by

$p = \frac{RT}{v-b} - \frac{a}{v^2}$

$d\epsilon = \left(T\frac{\partial s}{\partial v}\Big|_T - p\right)dv$

$= \left(T\frac{\partial s}{\partial v}\Big|_T - p\right)dv$

$\frac{\partial s}{\partial v}\Big|_T = \frac{\partial\epsilon}{\partial T}\Big|_v$

$\therefore d\epsilon = \left[T\frac{\partial p}{\partial T}\Big|_v - p\right]dv$

we have my equation for p

$\therefore$

$\frac{\partial\epsilon}{\partial T}\Big|_v = \frac{\partial}{\partial T}\left(\frac{RT}{v-b} - \frac{a}{v^2}\right)\Big|_v$

$= \frac{R}{v-b}$

$d\epsilon = \left[T\left(\frac{R}{v-b}\right) - p\right]dv$

$= \left[T\left(\frac{R}{v-b}\right) - \left[\frac{RT}{v-b} - \frac{a}{v^2}\right]\right]dv$

$= \frac{a}{v^2}dv$

$= \int_{0.001}^{0.04}\frac{a}{v^2}dv$

$-\frac{a}{v}\Big|_{0.001}^{0.04}$ $\quad a = 0.9395$ Pa·m^6/mol^2

$v_i = 0.001$ m^3/mol

$v_f = 0.04$ m^3/mol

$-0.9395\left(\frac{1}{0.04} - \frac{1}{0.001}\right)$

915 Pa·m^3/mol

915 J/mol

$\Delta\epsilon = \Delta q - \Delta w$ $\quad$ heat work done by gas ∴ -w

$= \Delta q + a\omega$

$\Delta w = \Delta\epsilon - \Delta q$

$= 915 - 600$